Development of High Performance of Silicon Type Anode Material for Lithium Ion Batteries by the Carbon Coating

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Graphite is the customary anode for lithium ion batteries with theoretical capacity of 372 mAh/g or volumetric capacity of 830 mAh/l. In order to increase the specific energy of lithium ion batteries, new anode materials with capacity higher than 372 mAh/g are urgently needed. Several new materials, especially SnO-based materials, have recently been reported as possible anode materials to replace carbon. But these materials have large irreversible capacity and their cycling performance is unsatisfactory.

It is known that Si can alloy with Li up to $Li_{4.4}Si$ at high temperature, which will correspond to a capacity of 4000 mAh/g. However the reversibility of normal Si powder is poor[1)]. The reason is in the volume change of the material during cycling. Most of current studies to improve the cycleability have focused on creating a composite microstructure [2)] or composite material[3)].

Recently, we have developed the carbon coated natural graphite by chemical vapor deposition method (CVD)[4)] and this is now commercially available. The anode material of carbon coated graphite showed much better electrochemical performance as an anode in both propylene carbonate-based and ethylene carbonate-based electrolyte than the bare natural graphite.

We have tried to carbon coated-Si material as an anode of LIB to improve the cycleability of Si anode. Carbon-coated silicon was prepared using the CVD technique by Mitsui Mining Co.. Benzene or toluene vapor and nitrogen carrier gas were fed into a reaction tube at 900-1000C in which silicon is placed. At such a high temperature, the benzene or toluene vapor flowed into the reaction tube, decomposed and deposited on the silicon surface as a carbon coating.

All experiments were carried out using coin cells. Silicon anode material was used in a following way. It was firstly mixed with 9.6 wt % solution of PVDF in NMP (anode active material:PVDF=1:1.16 by weight). The mixture was agitated until homogeneous mass obtained. It was paste on a mesh electrode (diameter 16 mm) and dried at 60^{o}C for 2 hours. After that the electrodes were pressed under 1.5 tons between two stainless steel plates and dried under vacuum for 8 hours at 130^{o}C. In all cases Li metal was used as a cathode. The electrolyte solution was 1 M $LiPF_6$ in EC:DMC (1:2 v/v).

Battery test were as follows. (i) The cells were discharged (Li insertion to Si) to 3mV at a constant current (3 mA/10 mg active material) constant voltage for 5 hrs., (ii) the cells were charged at a constant current (3 mA/10 mg active material) to 1.5V, (iii) After second cycle,
the discharge at a constant current and constant voltage to 50, 100 or 150 mV etc for 5 hrs, and charge to 1.5V with constant current were cycled.

Fig.1 shows the charge/discharge profile of pure silicon and carbon-coated silicon, respectively. The capacity and cycleability of pure silicon is extremely poor, but carbon-coated silicon has a larger capacity over than 800 mAh/g-active material with superior cycleability. Furthermore, the developed silicon material is much safer because the metallic lithium deposition may not occur because the lowest potential of charge is 100 mV.

Fig.2 shows the cycleability of developed silicon material between 0.1-1.5V cycling after 2nd cycle.

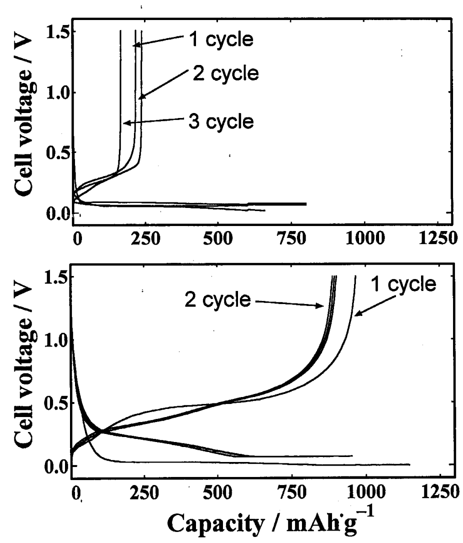

Fig.1 Typical charge/discharge behaviors of pure silicon (upper) and carbon-coated silicon (lower).

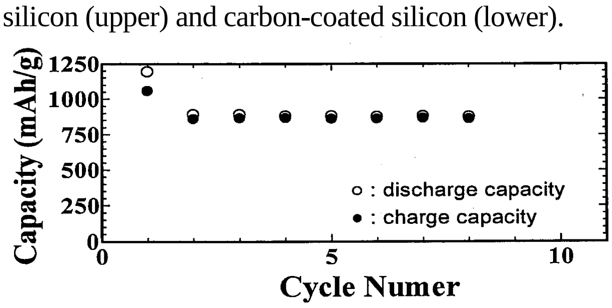

Fig. 2. Cycleability of carbon-coated silicon.

Previous studies showed that Li can form $Li_{22}Si_5$, $Li_{13}Si_4$, Li_7Si_3 and $Li_{12}Si_7$ at elevated temperatures. In our studies, we have used the first discharge capacity is limited to less than corresponding capacity of Li_7Si_3 (2230 mAh/g-Si) or $Li_{12}Si_7$ (1640 mAh/g-Si).

References

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